



(11)

EP 4 311 852 A1

(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:  
31.01.2024 Bulletin 2024/05

(51) International Patent Classification (IPC):  
**C10L 3/08 (2006.01)** **C10L 3/10 (2006.01)**  
**B01D 53/22 (2006.01)**

(21) Application number: 22187488.6

(52) Cooperative Patent Classification (CPC):  
**C10L 3/08; B01D 53/226; B01D 53/228;**  
**C10L 3/101; C10L 3/104; B01D 2053/221;**  
B01D 2256/245; B01D 2257/504; C10L 2290/10;  
C10L 2290/26; C10L 2290/46; C10L 2290/548

(84) Designated Contracting States:  
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB**  
**GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO**  
**PL PT RO RS SE SI SK SM TR**  
Designated Extension States:  
**BA ME**  
Designated Validation States:  
**KH MA MD TN**

(71) Applicant: **Paul Scherrer Institut**  
**5232 Villigen (CH)**

(72) Inventor: **Schildhauer, Tilman J.**  
**5200 Brugg (CH)**

(74) Representative: **Fischer, Michael**  
**Siemens AG**  
**Postfach 22 16 34**  
**80506 München (DE)**

## (54) PROCESS IMPROVEMENT UPGRADING IN POWER-TO-X (PTX) PROCESSES

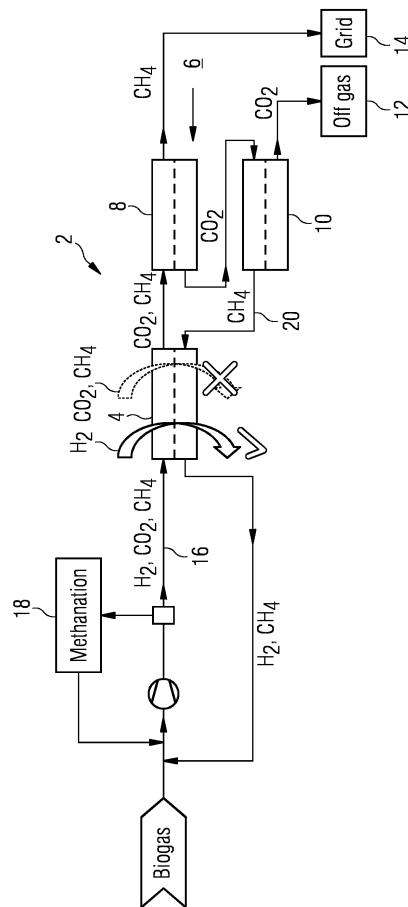
(57) Thus, the objective of the present invention is to provide a method and a system for the optimization of the part load capabilities of a biogas based PtX conversion that offer a better capability of using hydrogen that is generated or has not been used in the methanation process for further process steps, such as a recycling into the methanation process.

This objective according to the present invention by a method and a system (2) for the optimization of the part load capabilities of a biogas based PtX conversion, comprising:

- a) a fluidized bed reactor (18) enabled to convert biogas into a CH<sub>4</sub>-enriched product gas stream (16);
- a) a regular membrane upgrading unit (6) enabled to treat the CH<sub>4</sub>-enriched product gas stream (16) wherein the regular membrane upgrading unit (6) at least comprises a main membrane (8) being enabled to separate CO<sub>2</sub> from methane to yield injectable CH<sub>4</sub> enriched gas and a CO<sub>2</sub> cleaning membrane (10) being enabled to recover permeated methane downstream of the main membrane (8) from CO<sub>2</sub>; and
- c) a polymeric gas separation membrane (4) being enabled to treat the CH<sub>4</sub>-enriched product gas stream (16) wherein the polymeric gas separation membrane (4) is in addition to the regular membrane upgrading unit (6) and is positioned downstream of the fluidized bed reactor (18) and upstream of the regular membrane upgrading unit (6).

By the provision of the additional polymeric gas separation membrane, the method and the system allow to increase the recycle rate of hydrogen in the process and therefore reduce its loss through the off gas stream. At

the same time, the present invention also allows to decrease the slip of CH<sub>4</sub> through the same path and reduce the energy loss through the off gas stream.



## Description

**[0001]** The present invention is related to a method and a system for the optimization of the part load capabilities of a biogas based PtX conversion.

**[0002]** Biogas based PtX conversion processes are widely used. These processes will form part in the replacement of fossil fuel for the energy and/or heat generation. For the optimization of the operating conditions in methanation processes, an appropriate part load of the biogas with hydrogen is desired.

**[0003]** Thus, the objective of the present invention is to provide a method and a system for the optimization of the part load capabilities of a biogas based PtX conversion that offer a better capability of using hydrogen that is generated or has not been consumed in the methanation process for further process steps, such as a recycling into the methanation process.

**[0004]** This objective according to the present invention by a method according to claim 1 and a system according to claim 2. By the provision of the additional polymeric gas separation membrane, the method and the system allow to increase the recycle rate of hydrogen in the process and therefore reduce its loss through the off gas stream. At the same time, the present invention also allows to decrease the slip of CH<sub>4</sub> through the same path and reduce the energy loss through the off gas stream.

**[0005]** Preferred embodiments of the present invention are hereinafter described in more detail with reference to the drawing which depict in the figure a schematic view on a system 2 for biogas based PtX conversion. In order to further improve the part load capabilities of a biogas-based PtX process, the figure shows the introduce of a polymeric gas separation membrane 4 in addition to a regular membrane upgrading unit 6 that usually comprises a main membrane 8 (that separates CO<sub>2</sub> from methane to yield injectable gas for a gas grid 14) and a CO<sub>2</sub> cleaning membrane 10 (that recovers permeated methane from the CO<sub>2</sub> before it is vented with the off gas stream 12). The present invention allows thus to increase the recycle rate of hydrogen in the process at an early stage and therefore reduce its loss through an off gas stream 12. At the same time, the present invention also allows to decrease the slip of CH<sub>4</sub> through the same path and reduce the energy loss through the off gas stream 12.

**[0006]** The polymeric gas separation membrane 4 - also called hereinafter sweep membrane - can be applied in a raw product gas stream 16 coming from the methanation reactor 18 upstream of the regular membrane upgrading unit 6. Under favorable conditions, the polymeric gas separation membrane 4 separates at least a part of the hydrogen already before the raw product gas stream 16 enters the regular membrane upgrading system 6.

**[0007]** Furthermore, CO<sub>2</sub> may be transferred from the recycle stream to the retentate side. This leads to an accumulation of CO<sub>2</sub> and therefore a replacement of H<sub>2</sub> with CO<sub>2</sub> in the membrane upgrading unit 6.

**[0008]** A scheme for the sweep membrane process in-

dication the desired and undesired permeating flow in the sweep membrane is illustrated in the figure. The left arrow over the sweep membrane 4 represents the desired H<sub>2</sub> permeation (light-grey color) while the right arrow over the sweep membrane represents the blocking function of the sweep membrane 4 for the undesired permeation of CO<sub>2</sub> and CH<sub>4</sub> (dark-grey color).

**[0009]** This additional sweep membrane 4 is equipped with an inlet at the permeate side for a so-called sweep stream (see Figure). The recycle stream of the plant, corresponding to the retentate of the second upgrading stage in the membrane upgrading unit, directly forms the sweep-stream 20. The advantage of feeding the recycle stream as a sweep stream 20 to the permeate side is, that it lowers the partial pressure difference of CO<sub>2</sub> and CH<sub>4</sub>. Therefore, the permeation of these components in the sweep membrane 4 can be inhibited. On the other hand, as the H<sub>2</sub> content in the recycle stream is already decreased by the second membrane stage 10, the permeation of H<sub>2</sub> is favored. Therefore, under favorable conditions, it is possible to increase the selective recycling of H<sub>2</sub> without changing the membrane type.

**[0010]** In order to investigate the feasibility of this selective separation of H<sub>2</sub> and the benefits of a sweep stream on the membrane's performance, simulations as well as field tests were performed on the commercial biogas upgrading membrane. Both delivered promising results in this regard.

**[0011]** The polymeric gas separation membrane 4 can be made from polymers, such as poly-imide, poly-propylene etc. Ceramic and metallic membranes are often a bit more selective than polymeric membranes but they require significantly higher temperatures (as compared to ambient temperatures or slightly elevated temperatures above ambient temperature) and often also higher pressure gradients over the membrane.

**[0012]** The polymeric membranes further enables the operator of the system 2 to support the adjustment of specific selectivity of the permeation conditions by an appropriate adjustment of the content in the sweep gas stream 20 without losing any permeability for the desired H<sub>2</sub> permeation in the respective sweep membrane 4.

## Claims

1. A method for the optimization of the part load capabilities of a biogas based PtX conversion, comprising the steps of:

- 50 a) converting biogas in a fluidized bed reactor (18) into a CH<sub>4</sub>-enriched product gas stream (16);
- 55 a) treating the CH<sub>4</sub>-enriched product gas stream (16) by using a regular membrane upgrading unit (6) that at least comprises a main membrane (8) separating CO<sub>2</sub> from methane to yield injectable CH<sub>4</sub> enriched gas and a CO<sub>2</sub> cleaning

membrane (10) recovering permeated methane downstream of the main membrane (8) from CO<sub>2</sub>; and  
c) leading the CH<sub>4</sub>-enriched product gas stream (16) over a polymeric gas separation membrane (4) thereby positioning the polymeric gas separation membrane (4) in addition to the regular membrane upgrading unit (6) downstream of the fluidized bed reactor (18) and upstream of the regular membrane upgrading unit (6). 10

2. A system (2) for the optimization of the part load capabilities of a biogas based PtX conversion, comprising: 15

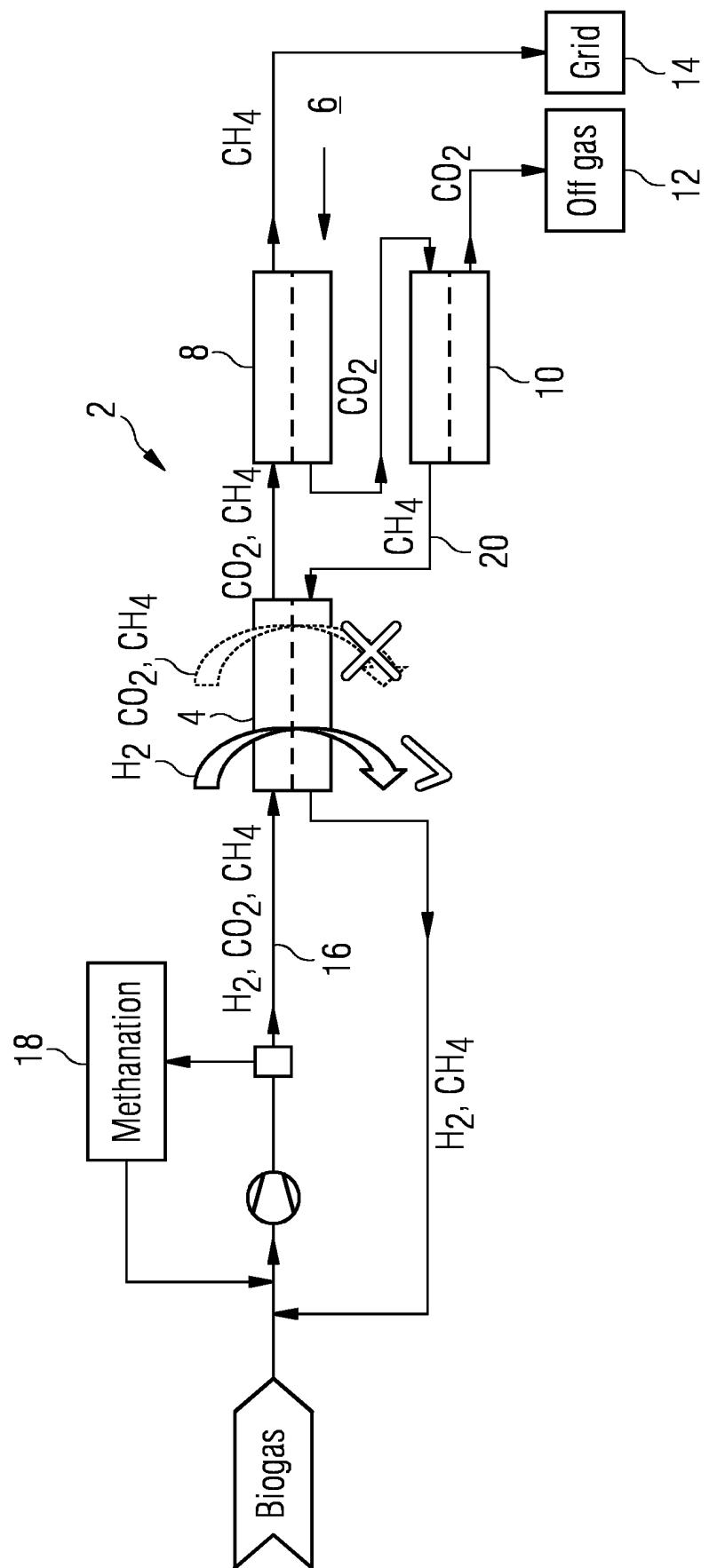
a) a fluidized bed reactor (18) enabled to convert biogas into a CH<sub>4</sub>-enriched product gas stream (16);  
a) a regular membrane upgrading unit (6) enabled to treat the CH<sub>4</sub>-enriched product gas stream (16) wherein the regular membrane upgrading unit (6) at least comprises a main membrane (8) being enabled to separate CO<sub>2</sub> from methane to yield injectable CH<sub>4</sub> enriched gas and a CO<sub>2</sub> cleaning membrane (10) being enabled to recover permeated methane downstream of the main membrane (8) from CO<sub>2</sub>; and  
c) a polymeric gas separation membrane (4) being enabled to treat the CH<sub>4</sub>-enriched product gas stream (16) wherein the polymeric gas separation membrane (4) is in addition to the regular membrane upgrading unit (6) and is positioned downstream of the fluidized bed reactor (18) and upstream of the regular membrane upgrading unit (6). 30 35

40

45

50

55





## EUROPEAN SEARCH REPORT

Application Number

EP 22 18 7488

5

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
10	<b>A</b> US 2019/381449 A1 (LIU CHUNQING [US] ET AL) 19 December 2019 (2019-12-19) * paragraphs [0006], [0007], [0010] – [0015], [0028] – [0036] * * figures * -----	1, 2	INV. C10L3/08 C10L3/10 B01D53/22
15	<b>A</b> WO 2012/048078 A1 (AIR LIQUIDE [FR]; KULKARNI SUDHIR S [US]; SANDERS JR EDGAR S [US]) 12 April 2012 (2012-04-12) * page 1, line 4 – line 22 * * page 2, line 32 – page 3, line 12 * * figure 1 * -----	1, 2	
20	<b>A</b> WITTE JULIA ET AL: "Direct catalytic methanation of biogas – Part II: Techno-economic process assessment and feasibility reflections", ENERGY CONVERSION AND MANAGEMENT, ELSEVIER SCIENCE PUBLISHERS, OXFORD, GB, vol. 178, 15 October 2018 (2018-10-15), pages 26–43, XP085524760, ISSN: 0196-8904, DOI: 10.1016/J.ENCONMAN.2018.09.079 * figures 2, 3 * -----	1, 2	
25			TECHNICAL FIELDS SEARCHED (IPC)
30			C10L B01D
35	<b>A</b> GANTENBEIN ANDREAS ET AL: "Flexible application of biogas upgrading membranes for hydrogen recycle in power-to-methane processes", CHEMICAL ENGINEERING SCIENCE, OXFORD, GB, vol. 229, 8 August 2020 (2020-08-08), XP086315247, ISSN: 0009-2509, DOI: 10.1016/J.CES.2020.116012 [retrieved on 2020-08-08] * abstract; figures 1, 5, 7 * -----	1, 2	
40			
45			
50	1 The present search report has been drawn up for all claims		
55	Place of search <b>Munich</b>	Date of completion of the search <b>22 December 2022</b>	Examiner <b>Keipert, Olaf</b>
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document			

ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.

EP 22 18 7488

5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

22-12-2022

10	Patent document cited in search report	Publication date	Patent family member(s)	Publication date
15	US 2019381449 A1	19-12-2019	EP 3806987 A1	21-04-2021
			US 2019381449 A1	19-12-2019
			WO 2019241722 A1	19-12-2019
20	-----			
25	WO 2012048078 A1	12-04-2012	EP 2624935 A1	14-08-2013
			US 2012111051 A1	10-05-2012
			WO 2012048078 A1	12-04-2012
30	-----			
35				
40				
45				
50				
55				

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82